

# Nonlinear Optical Response Functions of Mott Insulators Based on Dynamical Mean Field Approximation

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We investigate the nonlinear optical susceptibilities of Mott insulators with the dynamical mean field approximation. The two-photon absorption (TPA) and the third-harmonic generation (THG) spectra are calculated, and the classification by the types of coupling to external fields shows different behavior from conventional semiconductors. The direct transition terms are predominant both in the TPA and THG spectra, and the importance of taking all types of interaction with the external field into account is illustrated in connection with the THG spectrum and dc Kerr effect. The dependences of the TPA and THG spectra on the Coulomb interaction indicate a scaling relation. We apply this relation to the quantitative evaluation and obtain results comparable to those of experiments.

**KEYWORDS:** nonlinear optics, two-photon absorption, third-harmonic generation, dynamical mean field, electron correlation, Mott insulator

## 1. Introduction

Several nonlinear optical responses have been observed in Mott insulators; the two-photon absorption (TPA),<sup>1,2</sup> the third-harmonic generation (THG)<sup>3,4</sup> and the electroreflectance spectroscopy.<sup>5</sup> A notable point is that quasi one-dimensional (1D) Mott insulators show large nonlinear responses in these measurements, compared with those of conventional semiconductors. On the other hand magnitudes of nonlinear responses in two-dimensional (2D) systems are comparable to those of conventional semiconductors, and then the dimensionality dependence of nonlinear susceptibilities has also attracted attention in Mott insulators.<sup>2,4</sup> However this does not mean that the 2D system does not need an explanation, because the origins of the optical gap in the band insulators and Mott insulators are different from each other and the theory of conventional semiconductors does not apply to Mott insulators. There exists detailed comparison between experiments and theory in conventional semiconductors.<sup>6</sup> By contrast, optical nonlinearities in Mott insulators have not yet been understood to that level.

In the previous paper we derived the general formulation of the nonlinear optical susceptibility based on Green's function, and applied this to a calculation of the TPA spectrum of antiferromagnetic insulators with the Hartree-Fock approximation.<sup>7</sup> The dimensionality de-

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pendence of nonlinear susceptibilities was investigated and a semiquantitative estimation was made there. This calculation fails to include the damping effect, and the divergence arises at the band edge. This makes a quantitative estimation difficult and it is done with the averaged spectrum. (The damping effect is also important due to the experimental fact that the response time of Mott insulators is very fast.<sup>1)</sup>) Other approaches on nonlinear optical responses have been made with use of the numerical diagonalization method on small-sized systems.<sup>8</sup> This calculation consists of the discrete levels and dipole moments between them, and requires an artificial damping term. Although the qualitative reproduction of the dimensionality dependence is made with this method, even rough estimation of magnitudes of nonlinear susceptibilities is not attempted.

In this paper we study nonlinear susceptibilities of Mott insulators with the dynamical mean field approximation on the basis of the general formulation developed in ref.<sup>7</sup> The damping effect is naturally included within this method. We calculate the THG spectrum and dc Kerr effect as well as the TPA spectrum. It is shown that the direct transition term predominates in the TPA and THG spectra. This is not the case in the dc Kerr effect, but all types of processes are important in the same degree to form the oscillating structure. The scaling relations of the optical responses are derived, and the linear and nonlinear responses are proportional to the inverse of the square and the fourth power of the energy gap, respectively. According to this relation we obtain quantitative results of the TPA and THG spectra, which is comparable to experiments in the case that the value of the Coulomb interaction is somewhat larger than that of the bandwidth.

We present our formulation for calculation in §2, and the results are shown in §3. Several vertex corrections to the nonlinear susceptibilities are considered in Appendix. We set  $\hbar = c = 1$  and the electric charge  $e$  is not written explicitly. These are restored in quantitative calculations.

## 2. Formulation

Firstly we show how the Mott insulating state is described in our calculation. We apply the dynamical mean field approximation (DMFA) to the single-band Hubbard model,

$$\mathcal{H} = \sum_{\langle ij \rangle \sigma} t_{ij} (c_{i\sigma}^\dagger c_{j\sigma} + c_{j\sigma}^\dagger c_{i\sigma}) + U \sum_i n_{i\uparrow} n_{i\downarrow}. \quad (1)$$

( $t_{ij}$  is the transfer integral and  $U$  indicates the on-site Coulomb interaction.) We do not use the notation ‘theory’ which is usually used in the dynamical mean field theory (DMFT), but adopt ‘approximation’ because we do not consider the limit of the dimensionality  $d \rightarrow \infty$ . This implies the following. In DMFT the effective single-site action,

$$S_{\text{eff}} = - \int_0^\beta d\tau \int_0^\beta d\tau' \sum_\sigma c_\sigma^\dagger(\tau) \mathcal{G}_0^{-1}(\tau - \tau') c_\sigma(\tau') + U \int_0^\beta d\tau n_\uparrow(\tau) n_\downarrow(\tau) \quad (2)$$

is derived in the large dimension limit,  $d \rightarrow \infty$ .<sup>9</sup> ( $\beta = 1/T$  and  $T$  is the temperature.) In our case we use this effective action in arbitrary lattice systems. This means we neglect the higher-order terms of the transfer integral other than the first term of  $S_{\text{eff}}$ . This is the reason why we use DMFA instead of DMFT. In this case we do not need to scale the transfer integral by the factor of  $1/\sqrt{d}$ .

Other processes in the calculation are the same as in DMFT. The self-energy is calculated with  $S_{\text{eff}}$  as the functional of  $\mathcal{G}_0$ ,  $\Sigma[\mathcal{G}_0]$ . The Weiss function  $\mathcal{G}_0$  is calculated by the following relation,

$$\mathcal{G}_0^{-1}(\epsilon_n) = i\epsilon_n + \mu_0 - G^{(0)}(\epsilon_n) \quad (3)$$

and

$$G^{(0)}(\epsilon_n) = \sum_k \xi_k^2 G_k(\epsilon_n) - [\sum_k \xi_k G_k(\epsilon_n)]^2 / \sum_k G_k(\epsilon_n), \quad (4)$$

with Green's function,

$$G_k(\epsilon_n) = \frac{1}{i\epsilon_n - \xi_k + \mu - \Sigma(\epsilon_n)}. \quad (5)$$

(Here  $\epsilon_n = \pi T(2n - 1)$  and  $n$  is integer.) These functions are self-consistently determined, and the chemical potential  $\mu$ ,  $\mu_0$  is fixed by the condition,  $n_\sigma[G] = n_\sigma[\mathcal{G}_0] = 1/2$  (this sets the system to be half-filled). We make another approximation to solve  $S_{\text{eff}}$ . We calculate the self-energy within the second order perturbation,<sup>10</sup>

$$\Sigma(\epsilon_n) = -U^2 T^2 \sum_{n', l} \mathcal{G}_0(\epsilon_{n'}) \mathcal{G}_0(\epsilon_{n'} + \omega_l) \mathcal{G}_0(\epsilon_n - \omega_l). \quad (6)$$

We use the following dispersion relation,

$$\xi_k = -2t(\cos k_x + \eta \cos k_y) + 4t'\eta \cos k_x \cos k_y. \quad (7)$$

In numerical calculations below we put  $t = 1$  and fix the next-nearest-neighbor hopping  $t' = 0.2$  (results do not change if we vary  $t'$  moderately). We vary  $\eta$  as the dimensionality parameter from the 2D  $\eta = 1.0$  to the quasi 1D  $\eta = 0.1$ .

Next we present the formulation of the nonlinear optical response functions. The third-order nonlinear susceptibility is determined by,

$$\chi^{(3)}(\omega, \omega_1, \omega_2) = \frac{K^{(3)}(\omega, \omega', \omega'')}{\omega \omega_1 \omega_2 \omega_3}. \quad (8)$$

(The definitions of  $\chi^{(3)}$  and  $K^{(3)}$  are given in ref.<sup>7</sup>) Here,  $\omega = \omega_1 + \omega_2 + \omega_3$ ,  $\omega' = \omega_2 + \omega_3$  and  $\omega'' = \omega_3$ .  $\omega_1$ ,  $\omega_2$  and  $\omega_3$  are frequencies of the external fields and take different values depending on various methods of measurements.  $K^{(3)}$  is classified by the types of the coupling to the external fields as follows,

$$K^{(3)}(\omega, \omega', \omega'') = K_{<j4>}^{(3)} + K_{<j3>}^{(3)} + K_{<j2>}^{(3)}. \quad (9)$$

Each term is written as,

$$K_{<j4>}^{(3)} = \frac{2}{3!} \sum_k \int \frac{d\epsilon}{2\pi} v_k^4 \sum_{<i,j>} (G_a^R G_i^R G_j^R T_b + G_a^R G_i^R T_j G_b^A + G_a^R T_i G_j^A G_b^A + T_a G_i^A G_j^A G_b^A), \quad (10)$$

$$\begin{aligned} K_{<j3>}^{(3)} = & \frac{2}{3!} \sum_k \int \frac{d\epsilon}{2\pi} \frac{\partial v_k}{\partial k} v_k^2 \left[ \sum_i (G_a^R G_i^R T_b + G_a^R T_i G_b^A + T_a G_i^A G_b^A) + \sum_j (G_a^R G_j^R T_b + G_a^R T_j G_b^A + T_a G_j^A G_b^A) \right. \\ & \left. + \sum_{<i,j>} (G_i^R G_j^R T_b + G_i^R T_j G_b^A + T_i G_j^A G_b^A) \right], \end{aligned} \quad (11)$$

and

$$\begin{aligned} K_{<j2>}^{(3)} = & \frac{2}{3!} \sum_k \int \frac{d\epsilon}{2\pi} \left[ \left( \frac{\partial v_k}{\partial k} \right)^2 \sum_i (G_i^R T_b + T_i G_b^A) + \frac{\partial^2 v_k}{\partial k^2} v_k \sum_j (G_j^R T_b + T_j G_b^A) \right. \\ & \left. + \frac{\partial^2 v_k}{\partial k^2} v_k (G_a^R T_b + T_a G_b^A - G_b^R T_b - T_b G_b^A) \right]. \end{aligned} \quad (12)$$

Here  $G_x^{R,A} = G_k^{R,A}(\epsilon_x)$  ( $R$  and  $A$  mean the retarded and advanced, respectively),  $T_x = \tanh(\epsilon_x/2T) \text{Im} G_k^R(\epsilon_x)$  and  $v_k = \partial \xi_k / \partial k$ .  $\epsilon_x = \epsilon + \omega_x$  and  $\omega_a = \omega_1 + \omega_2 + \omega_3$ ,  $\omega_b = 0$ ,  $\omega_i = \omega_1 + \omega_2$ ,  $\omega_1 + \omega_3$  or  $\omega_2 + \omega_3$ ,  $\omega_j = \omega_1$ ,  $\omega_2$  or  $\omega_3$ . The diagrammatic representations are given in Fig. 1 of ref.<sup>7</sup>; Fig. 1(a), (b) and (c,d,e) for  $K_{<j4>}^{(3)}$ ,  $K_{<j3>}^{(3)}$  and  $K_{<j2>}^{(3)}$ , respectively. In this formulation vertex corrections are omitted, and these are discussed in Appendix.

### 3. Results

#### 3.1 The analysis of spectrum

The numerical results shown below are calculated with eqs. (10,11,12). The vertex corrections are not included, which are small compared to these terms as indicated in Appendix.

The decomposition of  $\text{Im} K^{(3)}$  to  $\text{Im} K_{<j4>}^{(3)}$ ,  $\text{Im} K_{<j3>}^{(3)}$  and  $\text{Im} K_{<j2>}^{(3)}$  in the case of the TPA spectrum ( $\omega_1 = -\omega_2 = \omega_3 = \omega$ ) is shown in Fig. 1. (We fix the temperature  $T = 0.036$  hereafter, and this parameter is not considered to be important because of  $\omega, U, t \gg T$ .) The predominance of  $K_{<j2>}^{(3)}$  over  $K_{<j4>}^{(3)}$  and  $K_{<j3>}^{(3)}$  is peculiar to Mott insulators, in contrast with conventional semiconductors where  $K_{<j2>}^{(3)}$  vanishes except for the self-transition.<sup>11,12</sup> The existence of  $K_{<j2>}^{(3)}$  in the TPA spectrum depends on the origin of the gap,<sup>7</sup> and the difference in magnitude of three  $\text{Im} K^{(3)}$  is understood by writing expressions explicitly as follows.

$$\begin{aligned} \text{Im} K_{<j4>}^{(3)}(\omega, 0, \omega) = & \frac{4}{3} \sum_k \int \frac{d\epsilon}{2\pi} v_k^4 \left[ \left( \tanh \frac{\epsilon - \omega}{2T} - \tanh \frac{\epsilon + \omega}{2T} \right) I_{\epsilon+\omega} R_{\epsilon} I_{\epsilon-\omega} R_{\epsilon} \right. \\ & \left. + \left( \tanh \frac{\epsilon + \omega}{2T} - \tanh \frac{\epsilon}{2T} \right) I_{\epsilon+\omega} I_{\epsilon} (I_{\epsilon+\omega} I_{\epsilon} - R_{\epsilon+\omega} R_{\epsilon} - R_{\epsilon+2\omega} R_{\epsilon+\omega} - R_{\epsilon} R_{\epsilon-\omega}) \right]. \end{aligned} \quad (13)$$

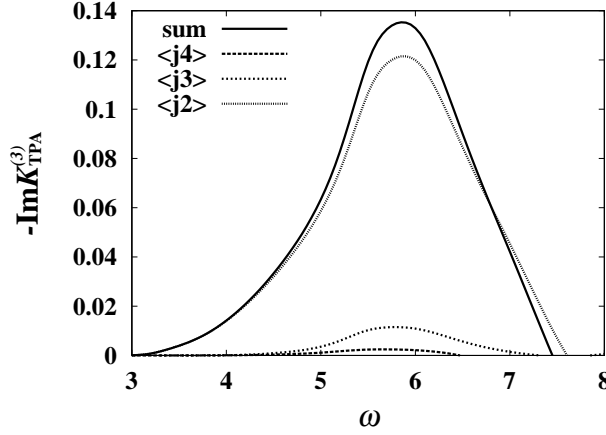


Fig. 1. The decomposition of  $\text{Im}K^{(3)}$  in the case of the TPA spectrum.  $U = 12$  and  $\eta = 0.2$  'sum' indicates the sum of three terms.

$$\begin{aligned} \text{Im}K_{<j3>}^{(3)}(\omega, 0, \omega) = & \frac{4}{3} \sum_k \int \frac{d\epsilon}{2\pi} \frac{\partial v_k}{\partial k} v_k^2 \left[ \left( \tanh \frac{\epsilon - \omega}{2T} - \tanh \frac{\epsilon + \omega}{2T} \right) I_{\epsilon+\omega} R_\epsilon I_{\epsilon-\omega} \right. \\ & \left. + \left( \tanh \frac{\epsilon}{2T} - \tanh \frac{\epsilon + \omega}{2T} \right) I_{\epsilon+\omega} I_\epsilon (R_{\epsilon+\omega} + R_\epsilon + R_{\epsilon+2\omega}/2 + R_{\epsilon-\omega}/2) \right]. \end{aligned} \quad (14)$$

$$\begin{aligned} \text{Im}K_{<j2>}^{(3)}(\omega, 0, \omega) = & \frac{1}{3} \sum_k \int \frac{d\epsilon}{2\pi} \left[ \left( \frac{\partial v_k}{\partial k} \right)^2 \left( \tanh \frac{\epsilon - \omega}{2T} - \tanh \frac{\epsilon + \omega}{2T} \right) I_{\epsilon+\omega} I_{\epsilon-\omega} \right. \\ & \left. + 2 \frac{\partial^2 v_k}{\partial k^2} v_k \left( \tanh \frac{\epsilon}{2T} - \tanh \frac{\epsilon + \omega}{2T} \right) I_{\epsilon+\omega} I_\epsilon \right]. \end{aligned} \quad (15)$$

Here  $I_\epsilon = \text{Im}G_k^R(\epsilon)$  and  $R_\epsilon = \text{Re}G_k^R(\epsilon)$ . We consider the case of  $\omega \simeq U/2$  in the TPA spectrum. These expressions indicate that the second terms of these three equations are small due to the factor  $I_{\epsilon+\omega} I_\epsilon = \text{Im}G_k^R(\epsilon + \omega) \text{Im}G_k^R(\epsilon)$ . (If one of  $\text{Im}G^R$  takes large values, the other has small values owing to the absence of the spectrum.) Then we consider the first terms in these expressions. The existence of  $R_\epsilon$  is the reason for the smallness of  $K_{<j4>}^{(3)}$  and  $K_{<j3>}^{(3)}$  compared with the direct transition term  $K_{<j2>}^{(3)}$ . The former two cases includes virtually excited states in the optical process, and  $R_\epsilon$  expresses this excitation. Although  $I_{\epsilon+\omega} I_{\epsilon-\omega} = \text{Im}G_k^R(\epsilon + \omega) \text{Im}G_k^R(\epsilon - \omega)$  can take large values around  $\epsilon \simeq 0$ ,  $R_\epsilon$  is roughly proportional to  $1/U$  in this region and is small. This explains results of Fig. 1.

The decomposition of  $K^{(3)}$  to  $K_{<j4>}^{(3)}$ ,  $K_{<j3>}^{(3)}$  and  $K_{<j2>}^{(3)}$  in the case of the THG spectrum ( $\omega_1 = \omega_2 = \omega_3 = \omega$ ) is shown in Fig. 2. The predominance of  $K_{<j2>}^{(3)}$  over  $K_{<j4>}^{(3)}$  and  $K_{<j3>}^{(3)}$  is the same as the case of the TPA spectrum, and the reason for this is also the same. (Here we consider the case of  $\omega \simeq U/3$ .) If we write the expressions of  $K^{(3)}$  explicitly, we can find that the factor like  $\text{Im}G_k^R(\epsilon + 3\omega) \text{Im}G_k^R(\epsilon)$  exists in  $K_{<j2>}^{(3)}$ . Then  $K_{<j2>}^{(3)}$  takes larger values than the other two terms, which include the nonresonant  $R_\epsilon$  term. In the THG spectrum the existence of the real part  $\text{Re}\chi^{(3)}$  makes it inevitable to calculate all three terms of  $K^{(3)}$  consistently,

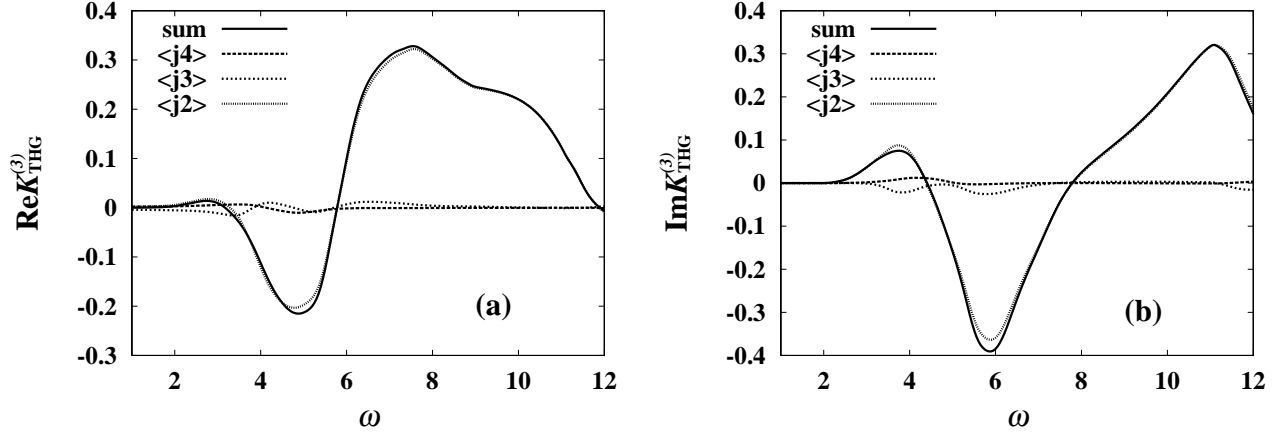


Fig. 2. The decomposition of (a) the real and (b) imaginary part of  $K^{(3)}$  in the case of the THG spectrum.  $U = 12$  and  $\eta = 0.2$ . 'sum' indicates the sum of three terms.

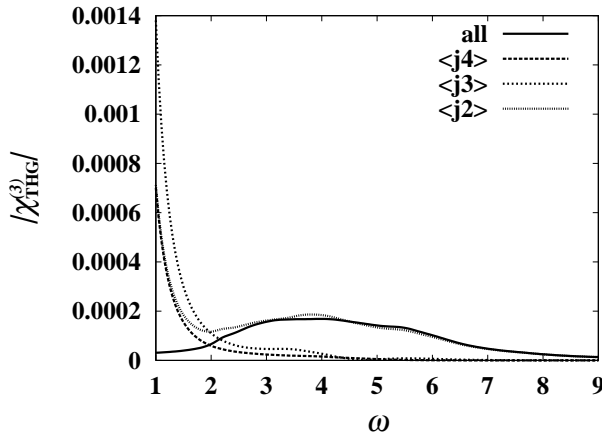


Fig. 3. The decomposition of  $|\chi_{\text{THG}}^{(3)}|$  in the case of the THG spectrum.  $|\chi_{<j4>}^{(3)}|$ ,  $|\chi_{<j3>}^{(3)}|$  and  $|\chi_{<j2>}^{(3)}|$  are calculated with  $K_{<j4>}^{(3)}$ ,  $K_{<j3>}^{(3)}$  and  $K_{<j2>}^{(3)}$ , respectively. 'all' means  $|\chi_{<j4>}^{(3)} + \chi_{<j3>}^{(3)} + \chi_{<j2>}^{(3)}|$ .  $U = 12$  and  $\eta = 0.2$ .

especially for small  $\omega$ . If we calculate  $|\chi_{\text{THG}}^{(3)}|$  only with  $K_{<j4>}^{(3)}$ ,  $K_{<j3>}^{(3)}$  or  $K_{<j2>}^{(3)}$  separately, each of  $|\chi_{<j4,j3,j2>}^{(3)}|$  diverges at small  $\omega$  as shown in Fig. 3. The cancellation among three  $K_{<j4,j3,j2>}^{(3)}$  occurs at small  $\omega$ , and we obtain convergence only if the summation of these three terms is taken. (This cancellation is the nonlinear analogue of that between the paramagnetic and diamagnetic terms in the linear response. It is unaffected by vertex corrections owing to the absence of the momentum-dependence in the self-energy.) This shows the importance of taking all three terms into account. The convergent behavior is related to that of the Drude weight, which is defined as  $D := \pi\omega\text{Im}\sigma|_{\omega\rightarrow 0}$  ( $\sigma$  is the conductivity) and  $D = 0$  for  $T \rightarrow 0$  in insulators.<sup>13</sup> The nonlinear correction is written as  $\text{Im}\sigma^{(3)} = -\text{Re}K^{(3)}/\omega^3$ . Therefore the nonlinear correction to the Drude weight would be divergent if  $\text{Re}K^{(3)}$  took finite values.

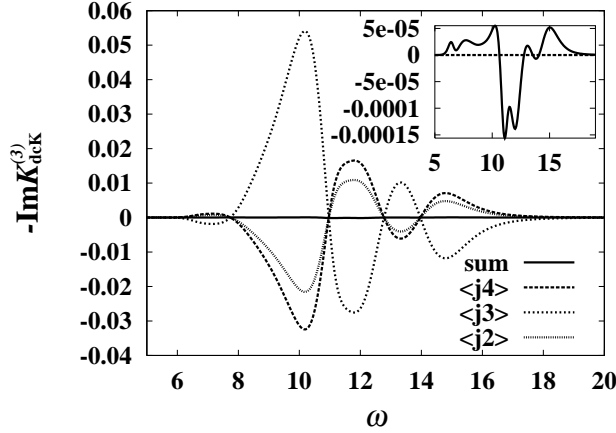


Fig. 4. The decomposition of  $\text{Im}K^{(3)}(\omega, 0, -\Delta\omega)$ .  $\Delta\omega = 0.05$ ,  $U = 12$  and  $\eta = 0.2$ . 'sum' indicates the sum of three terms and the inset shows this result separately because of the difference in scales.

(Strictly speaking, the term which is proportional to  $\exp(-E_g/T)$  ( $E_g$  is the energy gap) remains as in the linear response, but this is vanishingly small for  $E_g \gg T$ .)

The decomposition of  $\text{Im}K^{(3)}$  to  $\text{Im}K_{<j4>}^{(3)}$ ,  $\text{Im}K_{<j3>}^{(3)}$  and  $\text{Im}K_{<j2>}^{(3)}$  in an approximate case of the dc Kerr effect ( $\omega_1 = \omega$ ,  $\omega_2 = -\omega_3 = \Delta\omega$ ) is shown in Fig. 4. (It should be  $\Delta\omega \rightarrow 0$ , but we apply the finite difference to  $\chi^{(3)} = -K^{(3)}/(\omega^2\Delta\omega^2)$ .) In contrast to the above two cases, all of  $K_{<j4>}^{(3)}$ ,  $K_{<j3>}^{(3)}$  and  $K_{<j2>}^{(3)}$  contributes to  $K^{(3)}$  in the same degree. The reason for this is that  $\text{Re}G_k^R(\epsilon)$  does not necessarily locate at the nonresonant state, which is understood by writing the set of frequencies;  $(\omega_i, \omega_j) = (0, \Delta\omega)$ ,  $(0, -\Delta\omega)$ ,  $(\omega + \Delta\omega, \Delta\omega)$ ,  $(\omega + \Delta\omega, \omega)$ ,  $(\omega - \Delta\omega, -\Delta\omega)$ ,  $(\omega - \Delta\omega, \omega)$ . As shown in the inset the summation of these three terms is smaller than each of them by two orders of magnitude. All these terms are required to reproduce the characteristic oscillating structure similar to that observed in the electroreflectance spectroscopy.

It is known that sum rules hold in the nonlinear response.<sup>14,15</sup> The relation,  $\int_0^\infty \omega \epsilon_2^{\text{NL}}(\omega, -\omega', \omega') d\omega = 0$  holds for the TPA spectrum. Here,  $\epsilon_2^{\text{NL}}(\omega, -\omega', \omega')$  is the imaginary part of the complex dielectric function. If we treat the above three terms of  $K^{(3)}$  separately, we will violate this relation. The appearance of the oscillating structure in the dc Kerr effect as shown above is another example of the necessity to consider all these terms in  $K^{(3)}$  ( $\omega' = \Delta\omega$  in this case). A previous calculation do not take these terms into account properly.<sup>16</sup> They neglect the predominant term  $K_{<j2>}^{(3)}$ , and also fail to treat the divergence at small frequency region carefully in a calculation of the real part of  $\chi_{\text{THG}}^{(3)}$ .

### 3.2 The dependences of nonlinear susceptibilities on the Coulomb interaction

We show the dependences of the nonlinear susceptibilities on  $U/t$ ,  $U/W$  and  $\eta$ . (Here  $W$  is the bare bandwidth and is a function of  $t'$  and  $\eta$ .) The dependence of the integral of the linear absorption spectrum ( $\bar{\alpha} = \int \omega \text{Im}\chi^{(1)}(\omega) d\omega$ ) on  $t/U$ ,  $W/U$  with several values

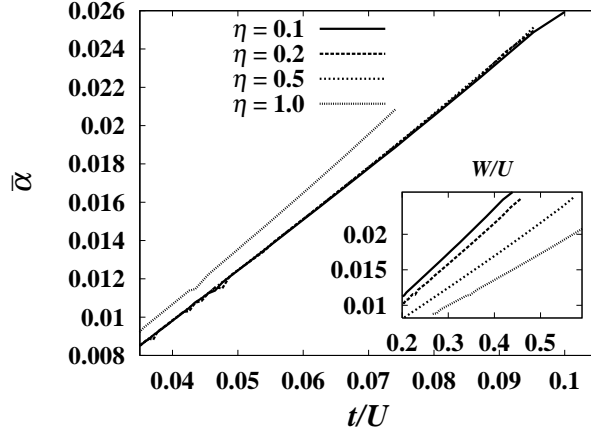


Fig. 5. The dependence of  $\bar{\alpha} = \int \omega \text{Im}\chi^{(1)}(\omega) d\omega$  on  $t/U$ . The inset shows the dependence of the same quantities on  $W/U$ .

of  $\eta$  is shown in Fig. 5. (The value of  $U$  at which the Mott transition occurs depends on  $\eta$ , and these are  $U \simeq 9.1, 9.2, 10.2, 13.1$  for  $\eta = 0.1, 0.2, 0.5, 1.0$ , respectively.) The relation  $\bar{\alpha} \propto 1/U$  holds, which is consistent with the sum rule for the linear absorption.<sup>17</sup> If we put the lattice constant  $a = 5 \text{ \AA}$  and  $U = 2 \text{ eV}$  (The reason why we take this value is that the linear absorption spectrum in experiments peaks around this energy and in our simple model the spectrum always has the peak around  $U$ ), we get  $\alpha^{(1)}|_{\text{peak}} \simeq 0.98, 0.76 \times 10^5 \text{ cm}^{-1}$  at  $U = 13.5$  for  $\eta = 0.1, 1.0$ , respectively (here  $\alpha^{(1)}(\omega) = 4\pi\omega \text{Im}\chi^{(1)}(\omega)/c$  and  $c$  is the velocity of light which is written explicitly for the quantitative estimation). These are almost comparable to the results of experiments which are  $\alpha^{(1)}|_{\text{peak}} \simeq 4, 1 \times 10^5 \text{ cm}^{-1}$  in quasi 1D and 2D systems, respectively.<sup>2</sup> The relation  $\omega \text{Im}\chi^{(1)} \propto 1/U$  indicates that we expect a moderate enhancement of  $\alpha^{(1)}$  for smaller  $U$ .

The dependences of the peak of the TPA spectrum ( $\text{Im}\chi_{\text{TPA}}^{(3)}$  multiplied by  $\omega$ ) on  $t/U$  and  $W/U$  are shown in Fig. 6. The relation  $\omega \text{Im}\chi_{\text{TPA}}^{(3)} \propto 1/U^3$  holds approximately. (It deviates slightly from  $1/U^3$  for smaller  $U$ , and the results are rather proportional to  $1/U^{3.5}$ . This is because the peaks of the TPA spectrum shift to lower energies.) If we put the lattice constant  $a = 5 \text{ \AA}$  and  $U = 2 \text{ eV}$ , we get  $\text{Im}\chi_{\text{TPA}}^{(3)} \simeq 0.0155, 0.0133 \times 10^{-9} \text{ esu}$  at  $U = 13.5$  for  $\eta = 0.1, 1.0$ , respectively. If we extrapolate the relation  $\text{Im}\chi_{\text{TPA}}^{(3)} \propto 1/U^4$  for smaller  $U$ , we will obtain  $\text{Im}\chi_{\text{TPA}}^{(3)} \simeq 1.0, 0.1 \times 10^{-9} \text{ esu}$  at  $U = 4.76, \eta = 0.1$  and  $U = 8.15, \eta = 1.0$ , respectively.

The dependences of the peak of the THG spectrum on  $t/U$  and  $W/U$  are shown in Fig. 7. The relation  $|\chi_{\text{THG}}^{(3)}| \propto 1/U^4$  holds. If we set parameters same as above to evaluate  $|\chi_{\text{THG}}^{(3)}|$  quantitatively, we get  $|\chi_{\text{THG}}^{(3)}| \simeq 0.0217, 0.0162 \times 10^{-9} \text{ esu}$  at  $U = 13.5$  for  $\eta = 0.1, 1.0$ , respectively. If we assume that the relation  $|\chi_{\text{THG}}^{(3)}| \propto 1/U^4$  holds for smaller  $U$ , we will obtain  $|\chi_{\text{THG}}^{(3)}| \simeq 1.0, 0.1 \times 10^{-9} \text{ esu}$ , at  $U = 5.18, \eta = 0.1$  and  $U = 8.56, \eta = 1.0$ , respectively.

These results indicate that the dependence of the susceptibility on  $\eta$  is rather weak, at



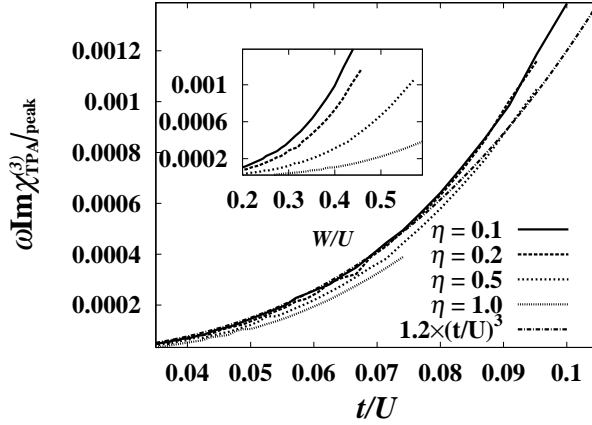


Fig. 6. The dependence of  $\omega \text{Im} \chi_{\text{TPA}}^{(3)} |_{\text{peak}}$  on  $t/U$ . The inset shows the dependence of the same quantities on  $W/U$ .

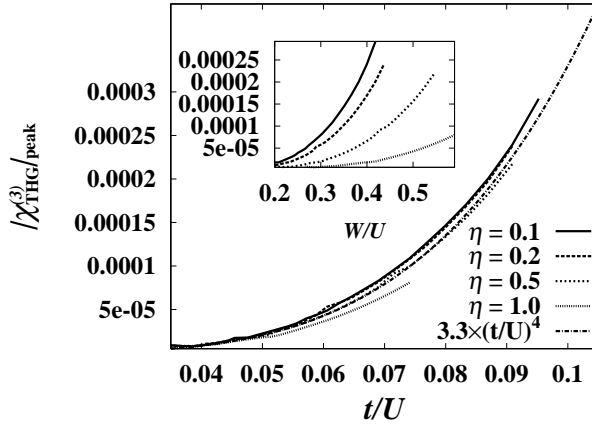


Fig. 7. The dependences of  $|\chi_{\text{THG}}^{(3)}|_{\text{peak}}$  on  $t/U$ . The inset shows the dependence of the same quantities on  $W/U$ .

least with  $t/U$  fixed. On the other hand it is strongly dependent on  $\eta$  in the case of  $W/U$  fixed, and this is because the bandwidth  $W$  is a function of  $\eta$ . The experimental results indicate that  $\chi^{(3)} \simeq 1.0, 0.1 \times 10^{-9}$  esu for quasi 1D and 2D systems, respectively.<sup>2,4</sup> Our calculation shows that it is possible to obtain  $\chi^{(3)}$  comparable to those of experiments in the case of  $U \gtrsim W$  (actually  $W = 4.4$  and  $8.0$  for  $\eta = 0.1$  and  $1.0$ , respectively). However this is based on the condition that we can extrapolate scaling relations for smaller  $U$ , and we discuss this point in §4. We find that the dependences of  $\chi$  on  $t'$  is weak with the moderate variation of  $t'$ .

In experiments the nonlinear susceptibility in the quasi 1D system is one order of magnitude larger than that in the 2D system. Our result does not show so much difference between  $\eta = 0.1$  and  $\eta = 1.0$  with fixed  $t/U$ . Although the improvement should be done on DMFA especially in quasi 1D systems, this is partly explained by the behavior of the density of states,

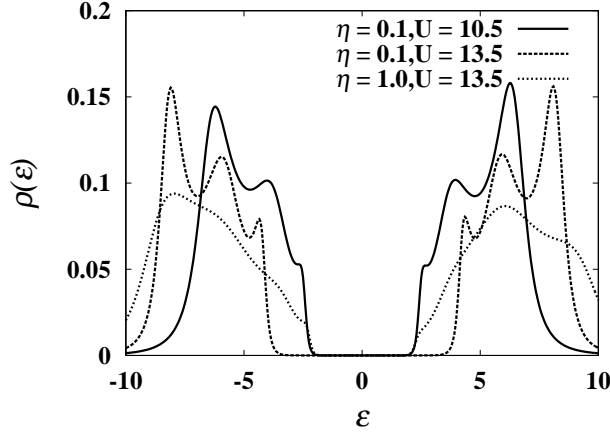


Fig. 8. The density of states  $\rho(\epsilon) = -\sum_k \text{Im}G_k^R(\epsilon)/\pi$  with several values of  $U$  and  $\eta$ .

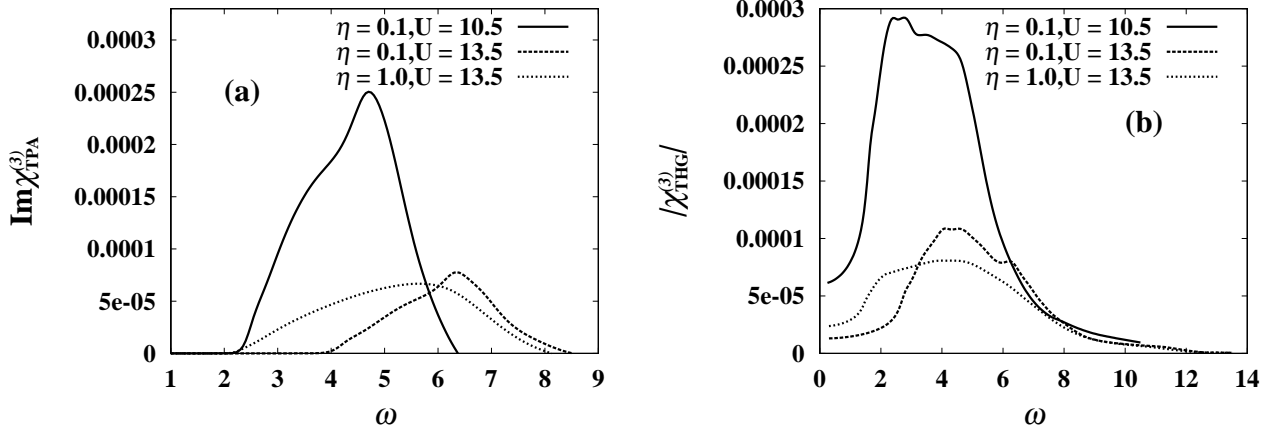


Fig. 9. (a)  $\text{Im}\chi_{\text{TPA}}^{(3)}$  and (b)  $|\chi_{\text{THG}}^{(3)}|$  with several values of  $U$  and  $\eta$ .

which is shown in Fig. 8. The experiment on the linear absorption spectrum indicates that the band-edges of the spectrum are almost same in both systems. This means that the nonlinear susceptibilities to be compared should have the same band-edge in the density of states. Therefore we compare the nonlinear susceptibilities at  $U = 10.5, \eta = 0.1$  and  $U = 13.5, \eta = 1.0$  as an example having such properties. The TPA and THG spectra are shown in Fig. 9. According the scaling relation  $\chi_{\text{TPA,THG}}^{(3)} \propto 1/U^4$ , a slight change of  $U$  brings about large variations in the nonlinear optical susceptibilities. On the other hand the linear absorption spectrum does not change considerably because of  $\chi^{(1)} \propto 1/U^2$ . Consequently the ratio of  $\chi^{(3)}|_{\eta=0.1}$  to  $\chi^{(3)}|_{\eta=1.0}$  becomes much larger than that of  $\chi^{(1)}|_{\eta=0.1}$  to  $\chi^{(1)}|_{\eta=1.0}$ , which resembles the observations in experiments.

The scaling relation in semiconductors shows that  $\chi_{\text{TPA}}^{(3)} \propto 1/E_g^4$ .<sup>6,12</sup> ( $E_g$  is the energy gap.) Although this is similar to our result, this does not mean that both Mott insulators

and conventional semiconductors obey the same scaling relation because the dominant terms in  $\chi^{(3)}$  are different between these materials as mentioned in §3.1. In spite of this fact, the difference in the magnitude of the nonlinear susceptibility between these materials is partly explained as follows. For the low dimensional systems the gap edge of the density of states is steeper than that of more high dimensional systems as shown in Fig. 8. This enhances the magnitude of the optical susceptibility in quasi 1D systems, compared to that conventional semiconductors.

#### 4. Summary and Discussion

We calculate nonlinear optical susceptibilities with DMFA on the basis of the general formulation of nonlinear response developed in a previous paper. The direct transition term is predominant in the TPA and THG spectra, which is contrary to conventional semiconductors. This is because the transition to the nonresonant intermediate states gives small contribution to  $\chi^{(3)}$  due to the strong correlation. On the other hand the origin of the band gap in semiconductors makes the direct transition negligible in  $\chi^{(3)}$ . In spite of these facts our result shows that as a function of the energy gap the scaling relation in Mott insulators behaves similarly as that of conventional semiconductors. A semiquantitative evaluation of nonlinear susceptibilities is carried out and shows that results are comparable to those of experiments on the condition that the value of the Coulomb interaction is somewhat larger than the bandwidth. The magnitude of  $\text{Im}\chi_{\text{TPA}}^{(3)}$  and  $|\chi_{\text{THG}}^{(3)}|$  takes similar values with each other, which is also indicated by experiments. These are not clarified in previous works for small systems which are diagonalized numerically. The scaling relation based on DMFA also shows that the smaller  $U$  is favorable to the larger  $\chi^{(3)}$  as in the Hartree-Fock calculation, which is contrary to the scenario of a large optical nonlinearity based on the spin-charge separation.<sup>8</sup> (The spin-charge separation holds approximately and is preferred at large  $U/t$ . The validity of the spin-charge separation as an explanation for the large optical nonlinearity can be judged partly from the dependence of  $\chi^{(3)}$  on parameters like  $U/t$ .)

One of our conclusions is dependent on the assumption that the scaling relation holds for smaller  $U$ . Here we discuss on this point and a possible modification. The main reason why the relations  $\chi^{(1)} \propto 1/U^2$  and  $\chi_{\text{TPA,THG}}^{(3)} \propto 1/U^4$  hold is as follows. By definition  $\chi^{(1)} \propto 1/\omega^2$  and  $\chi_{\text{TPA,THG}}^{(3)} \propto 1/\omega^4$ . This leads to the above  $U$ -dependences on the condition that the  $U$ -dependences of  $K^{(1)}$  and  $K_{\text{TPA,THG}}^{(3)}$  are weak and the optical gap scales with  $U$ . The calculation here indicates that this property holds at least within our approximation. However there is some room for improvement with respect to the description of the Mott insulator. The Hubbard model is considered to have the Mott transition at smaller values of  $U$  than those of a calculation presented here. This is the case especially in the model with  $\eta = 0.0$ , which is the 1D system and should be the Mott insulator even as  $U \rightarrow 0$ .<sup>18</sup> The improvement should be done on this point to examine the dimensionality dependences and the scaling relation for

smaller  $U$  (for example, an expansion to include  $k$ -dependence of the self-energy<sup>19</sup>).

### Acknowledgement

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### Appendix: Vertex corrections

The correction to vertices  $v_k$  and  $\partial^2 v_k / \partial k^2$  vanishes as in ref.<sup>20,21</sup> owing to the inversion symmetry. On the other hand it is not known to what extent the correction to vertices  $\partial v_k / \partial k$  and  $v_k^2$  contributes to  $\chi^{(3)}$ . The diagrams and equations of this type of vertices are similar to those of Fig. 1 (f,g,h) and §3.2 in ref.<sup>7</sup> The vertex correction to the predominant term in  $K^{(3)}$  is written as,

$$K_{\text{vc}}^{(3)}(\omega_l) = -T^2 \sum_{n,n'} \sum_k G_k(\epsilon_n + \omega_l) \frac{\partial v_k}{\partial k} G_k(\epsilon_n) \Gamma(\epsilon_n, \epsilon'_n; \omega_l) \sum_{k'} G_{k'}(\epsilon_{n'} + \omega_l) \frac{\partial v_{k'}}{\partial k'} G_{k'}(\epsilon_{n'}). \quad (\text{A}\cdot 1)$$

Here  $\Gamma(\epsilon_n, \epsilon_{n'}; \omega_l)$  is the reducible four-point vertex. If we consider the second-order perturbation term as an irreducible four-point vertex  $I(\epsilon_n, \epsilon_{n'}; \omega_l)$ , it is written as  $I(\epsilon_n, \epsilon_{n'}; \omega_l) = 2\chi(\epsilon_n - \epsilon_{n'}) + \phi(\epsilon_n - \epsilon_{n'})$  ( $\chi(\omega_l) = -U^2 T \sum_{k,n} G_k(\epsilon_n + \omega_l) G_k(\epsilon_n)$  and  $\phi(\omega_l) = -U^2 T \sum_{k,n} G_k(\omega_l - \epsilon_n) G_k(\epsilon_n)$ ). From the expression we anticipate that the vertex correction is small in the case that the dependence of  $I(\omega_l)$  on frequency is weak. It is because the particle-hole symmetry holds approximately. This can be verified by the numerical calculation which shows that the vertex correction is smaller than ordinary terms by two orders of magnitude.

In contrast to this, the nearest-neighbor interaction ( $V$ ) is considered to be important in optical responses because the excitons can be formed by the final-states interaction. Therefore we consider the vertex correction by the nearest-neighbor interaction. The formulation is similar to that of §3.2 in ref.<sup>7</sup> and we consider only the Fock term with this interaction. The vertex correction to the predominant term  $\text{Im}K_{<j2>}^{(3)}$ ,  $\text{Im}K_{<j2>}^{(3)}$  itself and the summation of both terms of the TPA spectrum are shown in Fig. A.1. The vertex correction shifts the spectrum to lower energy. This effect is rather small compared to that of antiferromagnetic insulators with the Hartree-Fock approximation because the damping effect is included in DMFA. Although the value of  $V/U$  is not known ( $V/U \simeq 0.22$  in Fig. A.1 is considered to be a large value), this type of the vertex correction will increase the values of  $\chi^{(3)}$  of §3.2 in some degree.

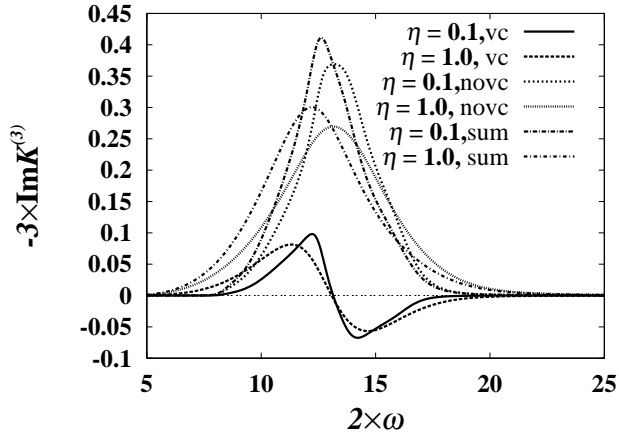


Fig. A-1. The vertex correction to  $K_{\text{TPA}}^{(3)}$  by the nearest-neighbor Coulomb interaction  $V$  with the Fock approximation.  $U = 13.5$  and  $V = 3.0$ . 'vc' and 'no vc' means the vertex correction term and  $\text{Im}K_{\text{TPA}}^{(3)}$  without the vertex correction, and 'sum' means the summation of both terms. The vertical and horizontal axes are scaled with three times and twice values, respectively.

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